NEW SYNTHETIC ROUTES TO BORON CAGE COMPOUNDS

FINAL REPORT

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February 10, 1985

U. S. ARMY RESEARCH OFFICE

DAAG29-82-K0005

UNIVERSITY OF PENNSYLVANIA

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AD-A153 537

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) New Synthetic Routes to Boron Cage Compounds		5. TYPE OF REPORT & PERIOD COVERED Final 11/15/81-11/15/84
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Larry G. Sneddon		8. CONTRACT OR GRANT NUMBER(s) DAAG29-82-K0005
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Pennsylvania Department of Chemistry Philadelphia, PA 19104		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE February 10, 1985
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Boranes, Boron Hydrides, Carboranes, Boron

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This project was concerned with the development of new synthetic routes to polyhedral boron cage compounds. This work resulted in the development of new synthetic routes to several important classes of compounds, including small cage carboranes, alkenyl-substituted boranes and carboranes, large cage mono-carbon carboranes and multi-cage boranes and carboranes.

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Summary of Scientific Goals and Results

Polyhedral boron cage compounds have been recognized as having numerous potentially important practical applications due to their unique chemical and physical properties. Unfortunately this potential has been largely unrealized because of the non-selective, low yield synthetic methods required to obtain these compounds. The principle thrust of the work performed under ARO sponsorship was to investigate the fundamental processes involved in the formation of these types of compounds and to apply these techniques to the development of new high yield, low energy, selective synthetic routes.

Our work has demonstrated (1) new catalytic, high yield syntheses of alkenyl boranes and alkenyl carboranes (2) the high yield thermally initiated conversion of alkenylpentaboranes into small cage carboranes (2) new routes to large cage mono-carbon carboranes (3) new catalytic routes to multi-cage compounds and (4) the synthesis of a range of new hybrid cluster systems with unique structural properties.

These results have been described in detail in the publications and progress reprots listed below:

Publications:

1. A.J. Borelli, Jr., J.S. Plotkin and L.G. Sneddon, "Structural Characterization of 6:4',5'-[(η-C_5H_5)Co-2,3-$(CH_3)_2C_2B_4H_3$][2',3'-$(CH_3)_2C_2B_4H_5$]: A Coupled-Cage Cobaltacarborane Complex Containing a Three-Center Boron Linkage", **Inorg. Chem.**, 21, 1328-1331 (1982).

2. E.W. Corcoran, Jr. and L.G. Sneddon, "Transition Metal Promoted Reactions of Boron Hydrides 4. A One-Step Synthesis of the Coupled Cage Borane, 1:2'-$[B_5H_8]_2$", **Inorg. Chem.**, 22, 182 (1983).

3. R.J. Astheimer and L.G. Sneddon, "Pyrolysis Reactions of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$. Isolation of a New Four Carbon Carborane, $C_4B_7H_{11}$, and the Boron Carbon Bonded Dimer and Trimers of 1,5-$C_2B_3H_5$. Improved Synthesis of the Mixed Cage Carborane, 2':2'[1',5'-$C_2B_3H_4$][1,6-$C_2B_4H_5$]", **Inorg. Chem.** 22, 1928-1934 (1983).

4. R.P. Micciche, J.S. Plotkin and L.G. Sneddon, "Structural Characterization of 3':2-[2',4'-$C_2B_5H_6$][1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$]: A Coupled-Cage Cobaltacarborane Containing a Boron-Boron Linkage", **Inorg. Chem.**, 22, 1765-1768 (1983).

5. R.P. Micciche and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 3. Synthesis and Structural Characterization of an Arene-Ferracarborane Complex: 1-(η^6-$CH_3C_6H_5$)Fe-2,3-$(C_2H_5)_2C_2B_4H_4$", **Organometallics**, 2, 674-678 (1983).

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7. T. Davan, E.W. Corcoran and L.G. Sneddon, "Transition-Metal-Promoted Reactions of Boron Hydrides 5. Palladium Promoted Pentaborane(9)-Olefin Coupling Reactions: A New, Mild Synthetic Route to Alkenylpentaboranes", **Organometallics**, 2 1693-1694 (1983).

8. J.A. Anderson, R.J. Astheimer, J.D. Odom and L.G. Sneddon, "The Use of Nuclear Magnetic Resonance to Investigate Bonding Between Quadrupolar Nuclei. Boron-Boron Spin-Spin Coupling Constants in Linked Polyhedral Borane and Carborane Cages", **J. Amer. Chem. Soc., 106**, 2275-2283 (1984).

9. R.J. Astheimer and L.G. Sneddon, "Photochemical Reactions of Hexafluoroacetone with Pentaborane(9) and 2,4-Dicarbaheptaborane(7)", **Inorg. Chem.** 23, 3207-3212 (1984).

10. R.J. Micciche, J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 4. Direct Synthesis of (η^6-Arene)Ferracarborane Clusters From Alkynes and Boranes. Structural Characterization of Four Carbon (η^6-Arene)Metallacarboranes: 1-[η^6-$(CH_3)_6C_6$]Fe-4,5,7,8-$(CH_3)_4C_4B_3H_3$ and 2-[η^6-$CH_3C_6H_5$]Fe-6,7,9,10-$(CH_3)_4C_4B_5H_5$". **Organometallics, 3**, 1396-1402 (1984).

11. R.J. Micciche, J.J. Briguglio and L.G.Sneddon, "Metal Atom Synthetis of Metalla-Boron Clusters 5. Synthesis of the First (η^6-Arene)Metallaborane and (η^6-Arene)Metallaoxaborane Clusters. Structural Characterizations of 5-[η^6-$C_6(CH_3)_3H_3$]FeB_9H_{13} and 2-[η^6-$C_6(CH_3)_3H_3$]Fe-6-OB_8H_{10}" **Inorg. Chem.** 23, 3992-3999 (1984).

12. E.W. Corcoran, Jr. and L.G. Sneddon, "Transition Metal Promoted Reactions of Boron Hydrides 6. Platinum(II) Bromide Catalyzed Borane and Carborane Dehydrodimerization Reactions: A New Synthetic Route to Boron-Boron Linked Multi-Cage Boranes and Carboranes" **J. Amer. Chem. Soc. 106**, 7793-7800 (1984).

13. J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 6. Synthesis and Structural Characterization of a Coupled Diborane-Metallacarborane Cluster: 5:1',2'-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5]" **Organometallics**, in press.

14. R.J. Micciche, P.J. Carroll and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 7. Synthesis and Structural Characterication of an Open-Cage Triple-Decker Metallathiaborane Cluster 4,6-(η-C_5H_5)$_2$-Co_2-3,5-$S_2B_2H_2$" **Organometallics**, submitted.

15. J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 8. Synthesis of New Iron, Cobalt and Nickel Clusters Derived From 2,6-$C_2B_7H_{11}$. Structural Characterizations of 2-[η^6-$C_6(CH_3)_3H_3$]Fe-1,6-$C_2B_7H_9$, 6-[η^6-$C_6(CH_3)_3H_3$]Fe-9,10-$C_2B_7H_{11}$ and 5,7,8-$(CH_3)_3$-11,7,8,10-[η^3-$C_4(CH_3)_4H$]$NiC_3B_7H_7$" in preparation.

Progress Reports

No.

1. 1/1/82-6/30/82
2. 7/1/82-12/31/82
3. 1/1/83-6/30/83
4. 7/1/83-12/31/83
5. 1/1/84-6/30/84

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